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Dynamic reactivity profiles of helium and neon atoms interacting with an intense laser field

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Abstract : Time evolution of various reactivity parameters like chemical potential, hardness, electrophilicity, phase volume *etc.* has been studied for the helium and neon atoms when they interact with an external intense laser field, within a quantum fluid density functional framework. The tug-of-war between the classical nuclear Coulomb potential and the potential due to the external field is clearly manifested. Corresponding Rydberg state dynamics of helium atom provides important insights into the associated chaotic ionization.

Keywords : Quantum fluid density functional theory, chemical reactivity, atom-field interactions, chaotic ionization, Rydberg states

PACS Nos. : 31.15.Ar, 31.15.Ew, 34.50.Rk, 34.60.+z

1. Introduction

The investigations of laser-atom interactions brought out a number of hitherto unknown novel phenomena that are of interest for both, basic insight into atomic, molecular and solid state structures and for their practical applications in a large number of different fields of research like holography, fiber optics, telecommunication, material sciences, biology, plasma physics, thermonuclear fusion, and so on. The interaction of high intensity ($>10^{13}$ W/cm^2) laser with matter, including a wide range of possible applications from sub-femtosecond spectroscopy [1] to harmonic generation control [2] and the generation of laser pulses with well-defined properties, have been considered to be topics throughout the last decade.

In this area of investigations, three processes namely (i) induced and inverse bremsstrahlung or free-free transitions in a laser field, (ii) above threshold ionization and (iii) higher harmonic generation, turned out to be of particular interest.

By varying the parameters of the laser field, like frequency, intensity, polarization, pulse duration, stochastic properties, *etc.* as well as on the atomic species considered, the efficiency of the above processes can be controlled. We are interested in laser pulses of only a few optical cycles duration with peak intensities of the order of the atomic unit 3.5×10^{16} W/cm^2. In this region of parameter space, effects which stems from the short form of the laser pulse are to be expected. In such pulses, the ponderomotive potential [3] cannot be considered to have a constant value, but rather will be time-dependent and thus shifts the interaction process from multiphoton regime to the regime of tunnel-ionization [4] and back again during the duration of the pulse.

When an atom is placed in an intense laser field ($I \sim 10^{13}$ W/cm^2), the Coulomb potential in which the electrons are placed are greatly distorted [5] and a large part of the electron density is transferred towards the nucleus within a half optical cycle [6]. The electron-nucleus interaction in hydrogen atom is comparable to the force that is exerted by a laser field of intensity of 3.5×10^{16} W/cm^2 on an electron.

In this paper, we study the time evolution of various reactivity indices of helium and neon atoms when they are placed in an intense laser field. A quantum fluid density functional theory is made use of for this purpose.

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The theoretical background for the present work is given in Section 2, while Section 3 presents the numerical details. Results are discussed in Section 4 and finally Section 5 contains some concluding remarks.

2. Theoretical background

We have considered the atomic units ($|e| = m = \hbar = 1$) through out the paper. The dynamics of the ground state of helium and neon atoms in the presence of an intense laser field has been studied here. The computation is done using a time-dependent density functional theory (TDDFT) [7] which provides a suitable nonlinear nonperturbative approach for investigations of intense electronic excitations. The dynamics in the ground state has been studied using the concept of quantum fluid dynamics (QFD) [8] which contains two basic equations, *viz.*,

an equation of continuity,

$$\frac{\partial \rho}{\partial t} + \nabla \bullet (j) = 0 \tag{1}$$

and an equation of motion,

$$\frac{\partial j}{\partial t} = P[\rho(r,t)], \tag{2}$$

where $P[\rho(r,t)]$ is the three-component density functional whose functional form has been approximated taking the idea from DFT and the resultant scheme is known as quantum fluid density functional theory (QFDFT) [9]. To see the time evolution of the many-electron system, we have solved the following generalized nonlinear Schrödinger equation developed through the amalgamation of eqs. (1) and (2) as,

$$\left[-\frac{1}{2}\nabla^2 + v_{eff}(r,t)\right]\phi(r,t) = i\frac{\partial \phi(r,t)}{\partial t}; \quad i = \sqrt{-1}, \tag{3}$$

where

$$\phi(r,t) = \rho^{1/2}\exp(i\xi) \tag{4}$$

and

$$j(r,t) = [\phi_{re}\nabla\phi_{im} - \phi_{im}\nabla\phi_{re}] = \rho\nabla\xi, \tag{5}$$

$\xi(r,t)$ is the velocity potential.

This formulation of QFD is initiated by substituting the amplitude-phase decomposition of the time-dependent wavefunction, $\phi(r,t) = R(r,t)\exp[i\xi(r,t)/\hbar]$ into the time-dependent Schrödinger equation.

The one-electron effective potential which appears in eq. (3) can be written for the ground states of He and Ne as

$$v_{eff}(r,t) = \frac{\delta T_{NW}}{\delta \rho} \cdot \frac{\delta E_{xc}}{\delta \rho} - \frac{Z}{r} + \int \frac{\rho(r,t)}{|r-r'|}dr' + v_{ext}(r,t), \tag{6}$$

where T_{NW} represents non-Weizsäcker [10] part of the kinetic energy and E_{xc} denotes the exchange-correlation energy functional, respectively.

The external potential $v_{ext}(r,t)$ which arises from the interaction with the laser pulses polarized along the z-direction can be written within the dipole approximation as

$$v_{ext}(r,t) = \varepsilon(t)\sin(\omega t)\bar{z}. \tag{7}$$

To have a slow oscillation during and after the laser pulse being switched on, $\varepsilon(t)$ can be written in terms of the maximum amplitudes ε_0 and the switched on time t' as

$$\varepsilon(t) = \varepsilon_0 \frac{t}{t'} \quad \text{for} \quad 0 \le t \le t' \tag{8a}$$

$$= \varepsilon_0 \quad \text{otherwise.} \tag{8b}$$

For an N-electron system with total energy E, electronegativity [11] and hardness [12] can defined within the density functional [13] framework as

$$\chi = -\mu = -\left(\frac{\partial E}{\partial N}\right)_{v(r)} \tag{9}$$

and

$$= \frac{1}{2}\left(\frac{\partial^2 E}{\partial N^2}\right) = \frac{1}{2}\left(\frac{\partial \mu}{\partial N}\right)_{v(r)} \tag{10}$$

where μ is the chemical potential and $v(r)$ is the external potential of the system.

These two global parameters measure the response of the system subjected to a change in N at constant external potential.

Alternatively, the chemical potential [14] is defined as the total electrostatic potential at a point r_c, *viz.*,

$$\mu(t) = -\chi(t) = \int \frac{\rho(r,t)}{|r_c - r|}dr + v_{ext}(r,t) \tag{11}$$

with the condition

$$\frac{1}{2}|\nabla\xi|^2 + \frac{\delta T}{\delta \rho} + \frac{\delta E_{xc}}{\delta \rho}\Big|_{r=r_c} = 0. \tag{12}$$

The dynamics of the highly excited ($n = 25$) helium atom has been studied by solving the pertinent time-dependent

Schrödinger equation (TDSE) (in a.u.)

$$\left[-\frac{1}{2}\nabla^2 + v_{core}(r) + v_{ext}(r,t)\right]\psi(r,t) = i\frac{\partial\psi(r,t)}{\partial t};$$

$$i = \sqrt{-1}, \tag{13}$$

where

$$v_{core}(r) = v_n(r) + v_s(r) + v_p(r). \tag{14}$$

Here, we have treated the helium atom as a pseudo-one-electron system whose core electron provides an effective core potential $v_{core}(r)$. In eq. (14), $v_n(r)$ represents the coulomb potential between the unshielded helium nucleus and the Rydberg electron, $v_s(r)$ denotes the shielding potential [15] which is nothing but the work done in moving the Rydberg electron from infinity to a point r through the charge probability cloud associated with inner unperturbed $1s$ electron, and $v_p(r)$ is known as the core polarization [16] which is a correction to $v_s(r)$ due to polarization in the $1\tilde{s}$ wave function of the core electron by the Rydberg electron.

Another crucial diagnostic of quantum signature of classical chaos is the uncertainty product or phase volume [17,18] which represents the compactness of the electron cloud [19]. In the cylindrical polar coordinates, it is defined as

$$V_{ps} = \left\{\left\langle\left(p_\rho - \langle p_\rho\rangle\right)^2\right\rangle\left\langle\left(p_{\tilde{z}} - \langle p_{\tilde{z}}\rangle\right)^2\right\rangle\left\langle\left(\tilde{\rho} - \langle\tilde{\rho}\rangle\right)^2\right\rangle\left\langle\left(\tilde{z} - \langle\tilde{z}\rangle\right)^2\right\rangle\right\}^{1/2}. \tag{15}$$

Another quantity of great significance is the electrophilicity index (ω) [20]. This quantity (ω) measures the propensity to absorb electron. Parr *et al* [20] defined the electrophilicity in terms of chemical potential (μ) and chemical hardness (η) as

$$\omega = \frac{\mu^2}{2\eta}. \tag{16}$$

To obtain the harmonic spectra we made the Fourier transform of the induced dipole moment, $D^z_{ind}(t)$, to get $d(\omega)$. Since the experimental harmonic distribution is proportional to the absolute square of $d(\omega)$ [21], it has been treated likewise.

3. Numerical details

The generalized nonlinear Schrödinger equation (GNLSE) is solved using a leapfrog-type finite difference scheme [22]. In this problem we have used cylindrical polar coordinates $(\tilde{\rho}, \varphi, \tilde{z})$ system. Since the system has a cylindrical symmetry in the presence of an axial external field, the analytical integration is carried out over the azimuthal angle $0 \le \varphi \le 2\pi$. If we take $x = \sqrt{\tilde{\rho}}$ and $y = \tilde{\rho}\psi$ then equation (3) becomes

$$\frac{3}{4x^3}\frac{\partial y}{\partial x} - \frac{1}{4x^2}\left)\frac{\partial^2 y}{\partial x^2} - \frac{\partial^2 y}{\partial \tilde{z}^2} - \left\{\frac{1}{x^4} - 2\left(v_{core} + v_{ext}\right)\right\}y = 2i\frac{\partial y}{\partial t} \tag{17}$$

The resulting tridiagonal matrix equation is then solved using a Thomas algorithm with the initial and boundary conditions given below :

$$y(x,\tilde{z}) \text{ is known for } \forall\ x,\tilde{z} \text{ at } t = 0, \tag{18a}$$

$$y(0,\tilde{z}) = 0 = y(\infty,\tilde{z}) \quad \forall\ \tilde{z},t, \tag{18b}$$

$$y(x,\pm\infty) = 0 \quad \forall\ x,t. \tag{18c}$$

The temporal mesh size was taken as $\Delta t = 0.0125$ a.u. and the spatial grids are taken as $\Delta x = \Delta\tilde{z} = 0.05$ a.u.

For the study of the excited state of helium, we have solved the time-dependent Schrödinger equation (TDSE) using alternating direction implicit (ADI) method [22] with rest of the items as above. Mesh sizes adopted in this case are $\Delta x = \Delta\tilde{z} = 0.4$ a.u. and $\Delta t = 0.01$ a.u.

4. Results and discussion

The time evolution of electric fields for different field amplitudes (1.5 a.u. and 2.5 a.u.) and frequencies (1.5π a.u. and 3.0π a.u.) is shown in Figure 1. The black line, red line, blue line and green line indicate field amplitude

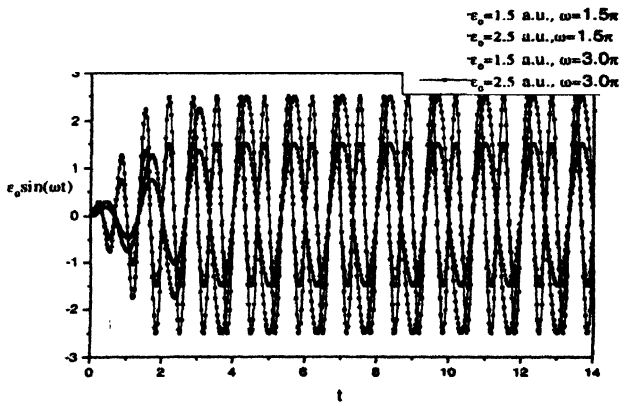

Figure 1. External electric field applied to the system.

1.5 a.u. and frequency 1.5π a.u., field amplitude 2.5 a.u. and frequency 1.5π a.u., field amplitude 1.5 a.u. and frequency 3.0π a.u. and field amplitude 2.5 a.u. and frequency 3.0π a.u., respectively.

In Figures 2 and 3, chemical potential profiles of helium and neon atoms in their ground states for different parameter values have been depicted. There is an in-phase oscillation of μ with the external electric field. For

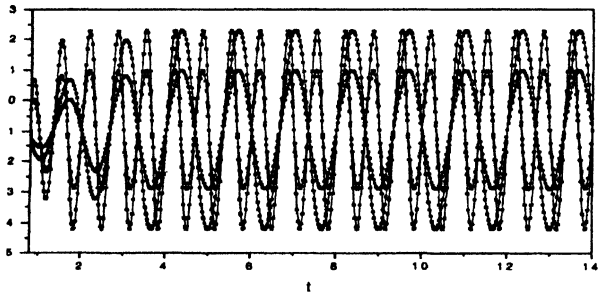

Figure 2. Chemical potential of helium ground state.

Figure 3. Chemical potential of neon ground state.

both the figures, greater the field amplitude, greater the magnitude of the chemical potential. It is also clear from the above figures that oscillation frequency of the chemical potential for external field with frequency 1.5π is half that of the oscillation frequency of the chemical potential for external field with frequency 3.0π.

Figures 4 and 5 represent the time evolution of chemical hardness (η) of the ground states of helium and neon atoms, respectively. The η is fluctuating albeit not in phase for both the cases. Increasing the value of the field intensity, we get higher chemical hardness values. However, for a super-intense laser field (intensity 12.64 a.u. and 50.00 a.u.), we get the in-phase oscillating behavior for η as well as μ, V_{ps} and ω for He (Figures 6–9) as well as Ne. The variation of μ is greater than that of η which implies that the degree of sensitivity of η is less than that of μ towards the external potential. As

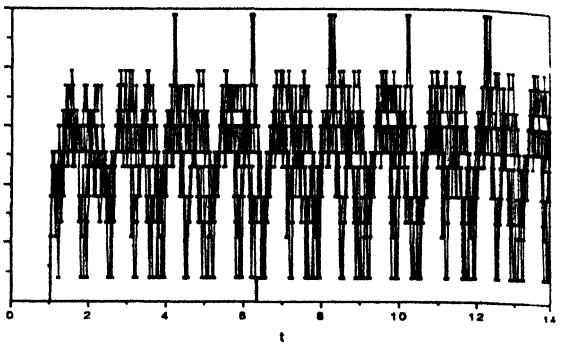

Figure 4. Chemical hardness of helium ground state.

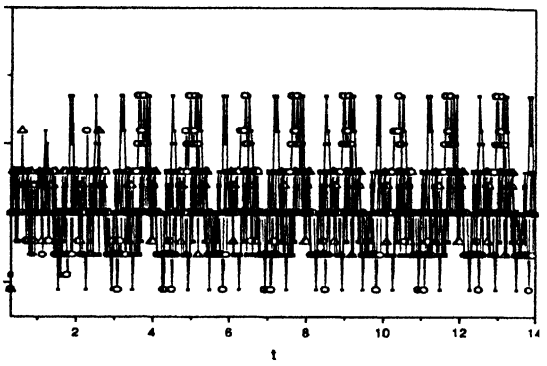

Figure 5. Chemical hardness of neon ground state.

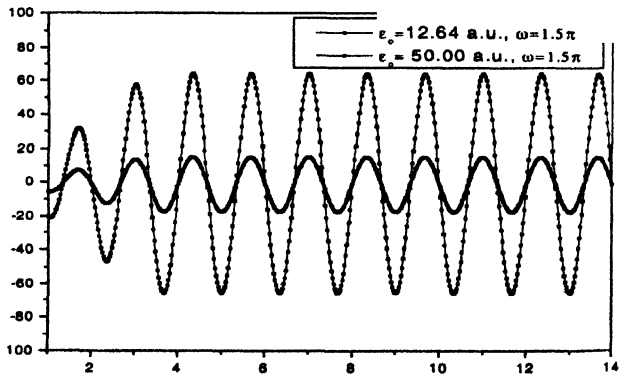

Figure 6. Chemical potential of helium ground state.

soon as the external field is switched on, the nuclear Coulomb field tries to keep the electron density spherical but the external field forces the electron density to be cylindrically symmetric. This tug-of-war between the nuclear Coulomb field and the external field is clearly manifested by the oscillation of the chemical potential (Figures 2 and 3). Since the chemical potential measures the first-order correction to energy and the chemical

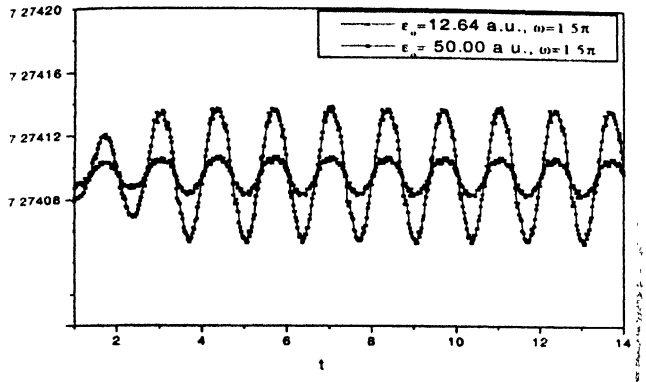

Figure 7. Chemical hardness of helium ground state.

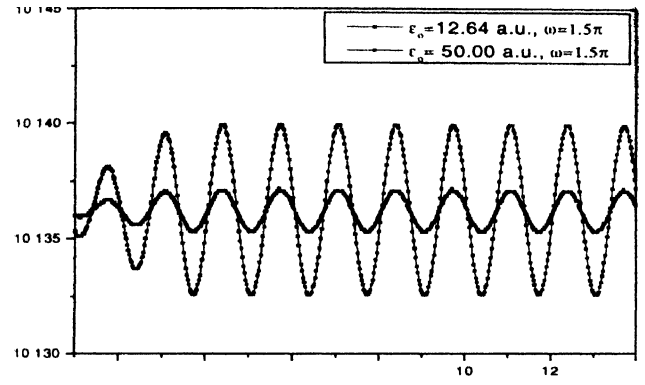

Figure 8. Phase volume of helium ground state.

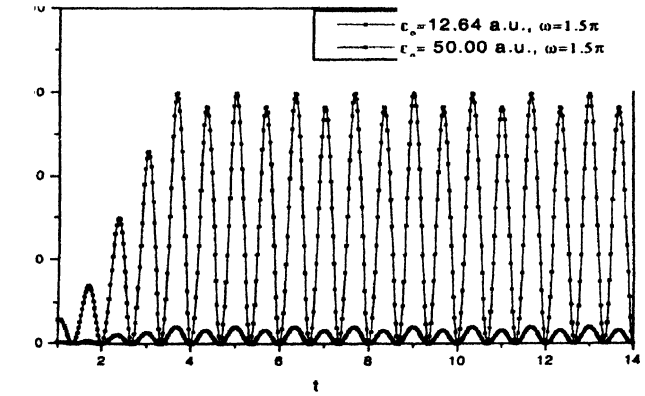

Figure 9. Electrophilicity of helium ground state.

hardness measures the second-order correction of energy, it is expected that the oscillation in hardness will take place in higher field strength which we see in super-intense laser field.

The phase volume of the ground states of helium and neon atoms are depicted in Figures 10 and 11, respectively. The phase volume of He is nearly in-phase but for Ne, it is completely in phase in nature. It is clear from Figure 11 that an increase in the frequency of the external field results in an increase in the frequency of oscillation of V_{ps} proportionally. The variation of the amplitude of the V_{ps} is also in proportion with that of the intensity of the external electric field. A clear cut in- phase oscillation is observed in the presence of a super-intense laser field.

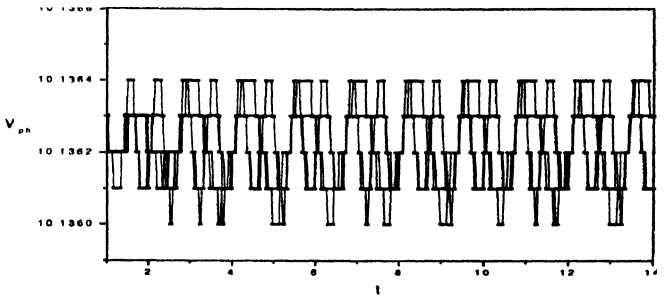

Figure 10. Phase volume of helium ground state.

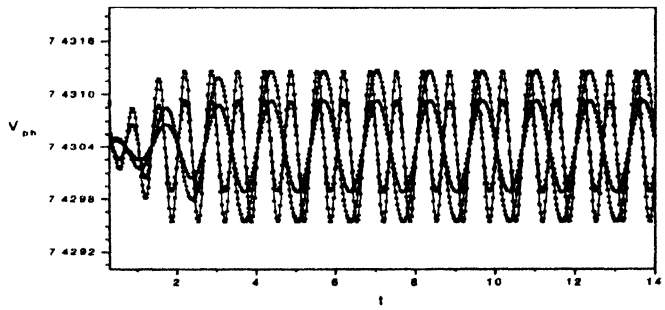

Figure 11. Phase volume of neon ground state.

The dynamic behavior of electrophilicity (ω) is presented in Figures 12 and 13 for He and Ne, respectively. The electrophilicity is higher for higher field intensity. The electrophilicity of helium ground state is lower in magnitude than that of the neon ground state. The in-phase oscillation of ω is also discernible especially for the neon atom.

The harmonic spectra of helium and neon ground states are presented in Figures 14 and 15, respectively. Characteristic oscillations and eventual leveling off are observed in these plots which is more conspicuous for He. The nature of the envelopes are same as that obtained by Erhard and Gross [23] using the square of the Fourier transform of the induced dipole moment within the time-dependent density functional framework.

The excited state calculation for the helium atom has been done by taking one electron in the Rydberg (n = 25) orbital and keeping the remaining electron in the 1s orbital.

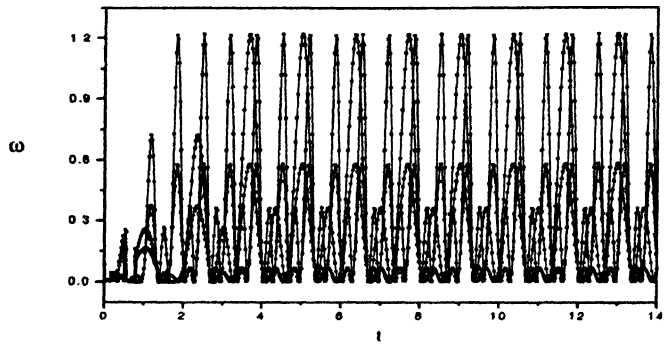

Figure 12. Electrophilicity of helium ground state.

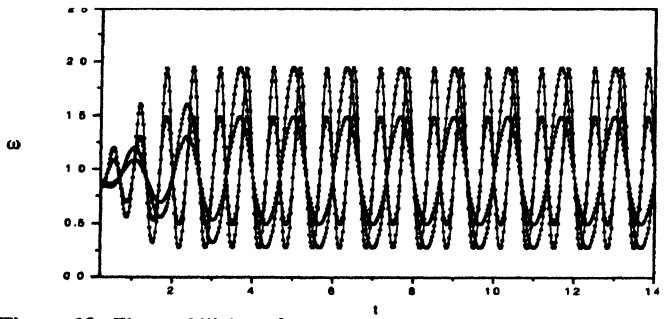

Figure 13. Electrophilicity of neon ground state.

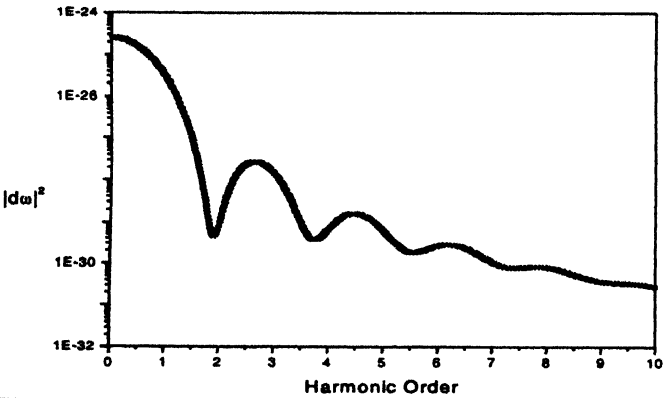

Figure 14. Harmonic spectra of helium ground state.

Figure 16 presents the time evolution of chemical potential for the excited state of He. The magnitude of μ increases with the amplitude of the external electric field. For the excited state, μ is fluctuating and its magnitude is greater than that of the He ground state. The in-phase oscillation of chemical potential is also absent in the excited state.

The time dependence of chemical hardness (η) of the He excited state is given in Figure 17. There is some oscillation in the η profile but it is neither in-phase nor steady throughout. If we compare the chemical hardness

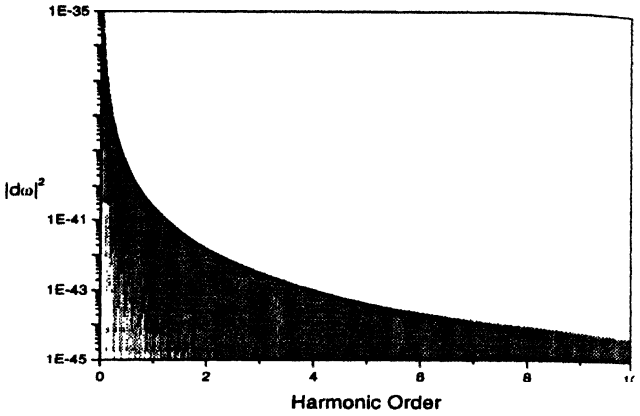

Figure 15. Harmonic spectra of neon ground state.

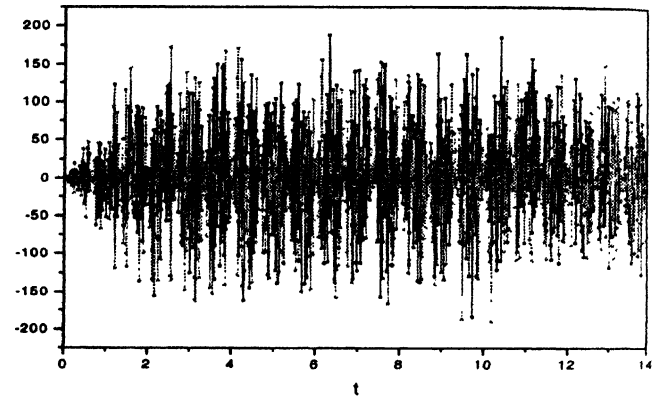

Figure 16. Chemical potential of helium excited state.

of He ground state (Figure 4) with chemical hardness of He excited state (Figure 17), we can see that the ground state has much higher chemical hardness than that of the excited state which is in conformity with the Maximum Hardness Principle (MHP) [24].

The excited state phase volume and electrophilicity

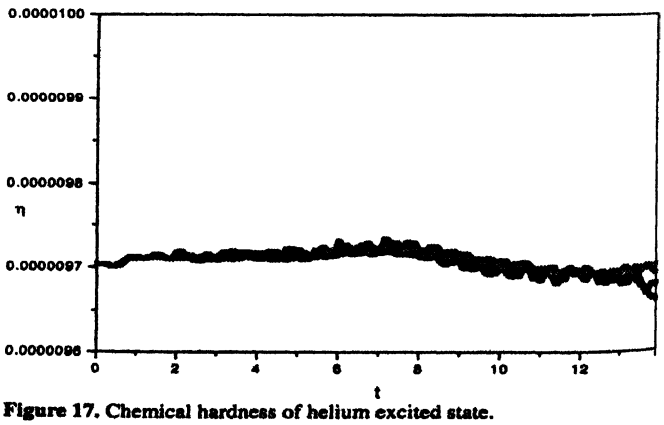

Figure 17. Chemical hardness of helium excited state.

index of He are presented in Figures 18 and 19, respectively. It is clearly delineated in Figure 18 that larger the value of the field intensity, larger the phase volume. Excited state phase volume (Figure 18) is also much higher in magnitude than that of the ground state (Figure 10). Similarly the

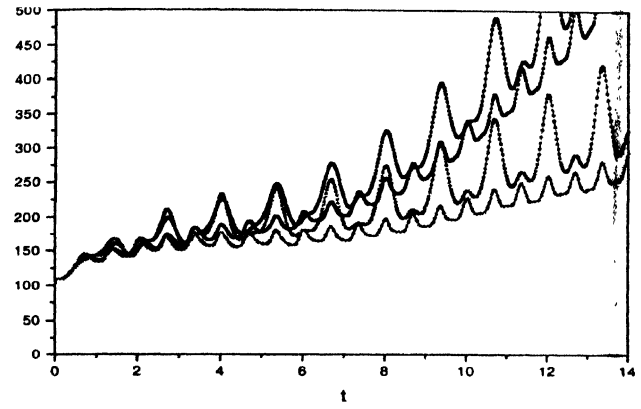

Figure 18. Phase volume of helium excited state.

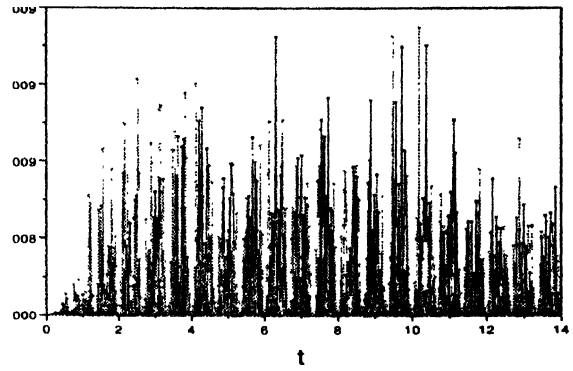

Figure 19. Electrophilicity of helium excited state.

signature of the characteristic chaotic ionization in this system.

Finally, the harmonic spectra of the excited state of He is presented in Figure 20. The intensity of the harmonic spectra of excited state (Figure 20) is more than that of the ground state (Figure 14) possibly originating from the larger chaoticity of the Rydberg state.

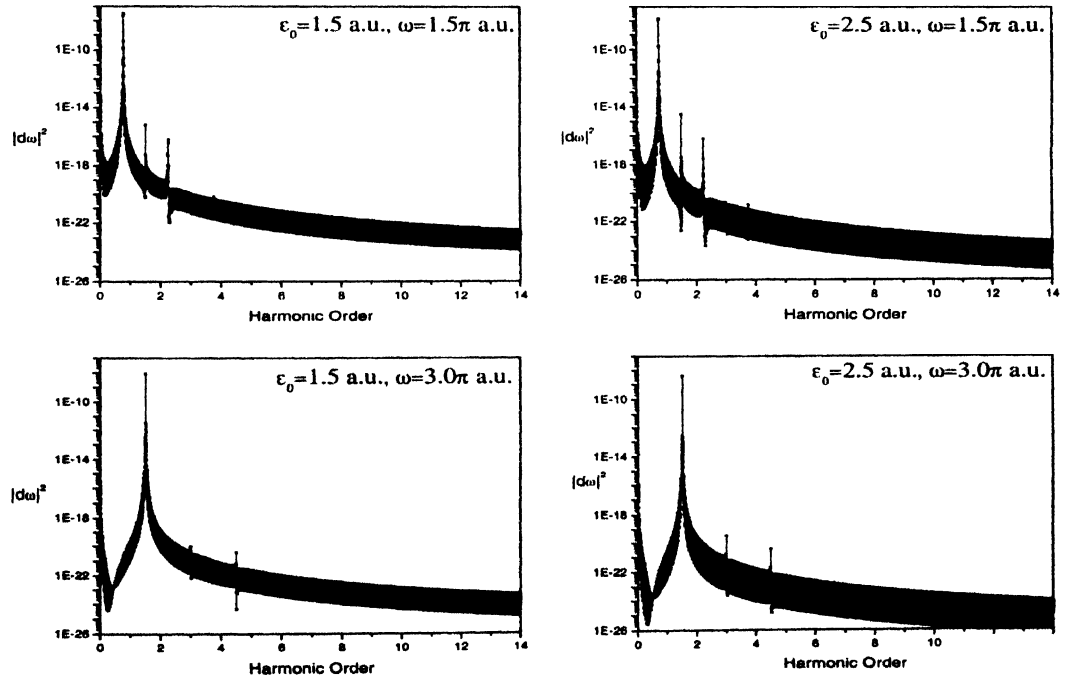

Figure 20. Harmonic spectra of helium excited state.

excited state electrophilicity (Figure 19) is greater than that of the ground state (Figure 12). Since the phase volume (uncertainty product) is considered as a measure of the quantum fluctuations [18], it can be considered as a

5. Conclusions

Dynamics of reactivity indices like chemical potential, chemical hardness, electrophilicity *etc.* for He and Ne atoms in their ground states interacting with external

intense and super-intense laser fields of different amplitudes and intensities, is studied within a quantum fluid density functional framework. Not all the quantities are equally sensitive to the external field and some of them require very high intensity field to exhibit in-phase oscillations. The overall dynamics is governed by the interplay of two potentials, *viz.*, the central Coulomb potential and the axial external potential. Some important insights into the Rydberg state dynamics of the helium atom is also obtained.

Acknowledgments

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